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(54) **Decor sheet for decorative laminate.**

(57) A decor sheet is useful in a decorative laminate includes cellulosic fibres, a sulfur dye and a precipitate of a basic salt. The salt and the dye are introduced to a papermaking furnish during the manufacture of the decor sheet. A decor sheet thus produced exhibits reduced deterioration after it is impregnated with a laminating resin. Alkaline earth metal hydroxides are the preferred basic-salt precipitates.

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The present invention relates to a decor sheet for a decorative laminate.

Decorative laminates are well known in the art. They are typically formed from a book of core sheets of kraft paper generally brown in colour and impregnated with a phenolic resin and at least one resin-impregnated decor sheet which is pigmented or coloured and disposed on at least one face of the book of core sheets. A resin-impregnated overlay may also be superimposed on the decor sheet for scratch resistance. These sheets are consolidated under heat and pressure into a laminate useful in covering walls, furniture, countertops, and the like.

In the past, decor sheets have been coloured using a class of dyes known as sulfur dyes. Decor sheets coloured with sulfur dyes have suffered from the drawback that the sulfur dye appears to accelerate the rate of cure of the resin to such an extent that the resin becomes highly crosslinked, brittle and exhibits poor postformability.

In accordance with a first aspect of this invention, we provide a decor sheet for use in a decorative laminate, said sheet including cellulosic fibres, a sulfur dye, and a precipitate of a basic salt.

The invention extends to decorative laminates incorporating such decor sheets.

The invention provides, in a second and alternative aspect thereof, a process for forming a decor sheet which comprises preparing a papermaking furnish of a cellulosic pulp, a sulfur dye, and a first water soluble and a second water soluble salt of a strong base, said first and second salts interacting to form a precipitate of a water insoluble basic salt; and forming a sheet from said furnish.

The term "water soluble" as used with respect to salts herein means that the salt is soluble in water in the amounts disclosed herein. For example, in the case of magnesium sulfate, the salt is sufficiently soluble in water to be added to the furnish for the decor sheet in an amount of 20-85% based on oven dry pulp.

The term "water insoluble" when used with respect to the precipitated salt herein means that the solubility of the precipitated salt in water is sufficiently low that at least a majority of the salt precipitates from solution under the conditions taught herein.

The term "salt" as used herein includes hydroxides.

As explained in more detail below, we introduce certain water insoluble basic salts and, more particularly, alkaline earth metal hydroxides to the papermaking furnish for the decor sheet. While not desiring to be bound by this as an explanation, these salts appears to precipitate on to the fibres in the furnish and to neutralize acidic groups in the sulfur dyes and thereby prevent the dyes from catalyzing curing of the resin.

The furnish for the decor sheet can be prepared from any cellulosic pulp including hardwood, softwood or mixtures of hardwood and softwood pulps. The pulp may be a chemical pulp such as a kraft pulp or a sulfite pulp, a chemi-mechanical pulp or a mechanical pulp. Alpha-cellulose such as cotton linter may be added to the furnish to further enhance postformability in a known manner.

Additives such as wet strength resins, retention aids, pH stabilizers, salting out agents, and alum may be used in a known manner to control end use characteristics.

A combination of water soluble salts is added to the furnish, which salts interact by ion exchange to precipitate a water insoluble basic salt in the furnish. In one arrangement, an alkaline earth metal salt such as magnesium sulfate is reacted with sodium hydroxide to precipitate magnesium hydroxide in the furnish.

An alkaline earth metal salt such as an alkaline earth metal sulfate or chloride (e.g. magnesium sulfate or magnesium chloride) is added to the furnish in an amount of about 20 to 85% by weight, all percents by weight herein being based on the oven dry weight of pulp in the furnish. It is anticipated that the amount of the alkaline earth metal salt will typically range from about 20 to 50% by weight. The amount of precipitated salt such as $Mg(OH)_2$ in the furnish is typically about 5 to 20% and more typically 5 to 12%.

To precipitate the basic salt in the furnish, a salt such as sodium hydroxide is added to the furnish. Preferably, this salt is added in an amount in excess of the stoichiometric amount required to precipitate the basic salt in the furnish. Sodium hydroxide is the water soluble base of choice and is generally added to the furnish in an amount of about 5 to 40% and preferably 15 to 25% by weight based upon the oven dry weight of the pulp in the furnish.

Sulfur dyes are well known in the art and commercially available. Some typical examples include C.I. Leuco Sulfur Black 1 Dye. The following dyes which are commercially available from Sandoz Corporation are useful herein: Sodyesul Black 4GCF, Sodyesul Black PLCF, Sodyesul Black 2RCF, Sodyesul Red 2B, and Hoechst Duasyn Thioblack SR, Duasyn Thiocarbon LP (C.I. Sulfur Black 1), etc.

The sulfur dye is preferably added to the furnish in its water soluble leuco form. The dye is typically added in an amount of about 10-30% based upon oven dry pulp. The amount will vary depending upon the decorative effect which is desired. Dyes added for tinting may be used in much lower amounts. To convert the dye from its soluble leuco form to its insoluble form and deposit the

dye onto the cellulosic fibres, an agent such as ferrous sulfate is used in a manner well known in the art. As is known, sulfur dyes are often supplied commercially in the leuco form in the presence of sodium sulfide which maintains them in that form. The ferrous sulfate interacts with the sulfide and causes the leuco dye to convert to its oxidized form. The sulfur dye can also be added in its oxidized form, converted to its leuco form by the addition of a reducing agent and reconverted to the oxidized form to deposit it on the fibres.

Because there is a tendency for sulfur dyes to oxidize over time and generate acidic groups which can degrade the paper, a pH stabilizer such as calcium carbonate may be added to the furnish in a known manner.

Any conventional laminating resin may be used with the decor sheet to form decorative laminates. Suitable laminating conditions including the selection of the resin, the amount of the resin, the temperature and pressure under which the laminate is consolidated, are all known in the art.

While the decor sheet is normally incorporated into a laminate such that it overlays the core sheets, the present decor sheet can be used at any location in the laminate in which its decorative effect is desired.For optimum postformability, we produce a decor sheet which exhibits a disc cure time, as defined in the following examples, of about 7 to 10 minutes.

The invention is illustrated in more detail by the following non-limiting examples:

Example 1

To a slurry of bleached hardwood kraft, bleached softwood sulfite, and second cut cotton linters at 4% consistency in water, 2% sodium carbonate, 4% calcium carbonate, 20% C.I. Leuco Sulfur Black 1 dye, 12% ferrous sulfate heptahydrate, 50% magnesium sulfate heptahydrate, 20% sodium hydroxide and 1% polyamide epichlorohydrin wet strength resin were added based upon pulp weight. This furnish was then diluted to 0.5% with water, adjusted to pH 10.0 with papermakers alum and formed into a fibrous mat by draining the suspension through a wire screen. The fibrous mat was then removed from the screen, placed between felts, pressed between steel rollers at 20 psi (1.379 x 10^5 N/m^2) and dried against a heated metal surface.

The paper thus produced was evaluated for its catalytic activity toward the crosslinking reaction of melamine formaldehyde resin as follows: Discs of 1.625 inch (4.1275 cm) diameter are die cut from the paper and weighed to the nearest milligram. The discs are individually placed with the wire side down between a 6 inch (15.24 cm) by 12 inch (30.48 cm) by 0.0015 inch (0.00381 cm) thick piece of foil which has been folded in half lengthwise polished side in. Powdered melamine formaldehyde resin of equal weight to the paper disc is spread evenly over the felt side of the disc using a spatula. This "sandwich" is then placed into a preheated (291°F + 0.5°) (143.89°C + 0.28°C) platen press. A pressure of 1000 psi (6.895 x 10^6 N/m^2) is applied for a preset time and then released. The "sandwich" is then removed from the press and placed between two metal blocks to rapidly cool the disc. The disc is then removed from the foil and placed into a boiling solution of 0.1% Rhodamine B dye in distilled water for 3 minutes. The disc is removed from the solution, blotted and allowed to air dry. Examination of the disc surface will indicate the state of cure of the resin. A distinct reddish colour is indicative of resin undercure, whereas a fully cured disc is not discoloured by the Rhodamine dye. This test is repeated at incremental pressing times to determine the time at which full resin cure is achieved. This time is designated as the disc cure time. The disc cure time for this example was found to be eight minutes.

Example 2

To a slurry of bleached hardwood kraft, bleached softwood sulfite, and second cut cotton linters at 4% consistency in water, 2% sodium carbonate, 4% calcium carbonate, 20% C.I. Leuco Sulfur Black 1 Dye, 12% ferrous sulfate heptahydrate, 85% magnesium sulfate heptahydrate, 20% sodium hydroxide and 1% melamine formaldehyde wet strength resin were added based upon pulp weight. This furnish was then diluted to 0.5% with water, adjusted to pH 8.0 with papermakers alum and formed into a fibrous mat by draining the suspension through a wire screen. The fibrous mat was then removed from the screen, placed between linter blotters, pressed between steel rollers at 20 psi (1.379 x 10^5 N/m^2), and dried against a heated metal surface. Disc cure time, six minutes.

Example 3

To a slurry of bleached hardwood kraft, bleached softwood sulfite, and second cut cotton linters at 4% consistency in water, 2% sodium carbonate, 4% calcium carbonate, 20% C.I. Leuco Sulfur Black 1 Dye, 12% ferrous sulfate heptahydrate, 85% magnesium sulfate heptahydrate, 15% sodium hydroxide and 1% melamine formaldehyde wet strength resin were added based upon pulp weight. This furnish was then diluted to 0.5% with water, adjusted to pH 8.0 with papermakers alum and formed into a fibrous mat by draining the

suspension through a wire screen. The fibrous mat was then removed from the screen, placed between linter blotters, pressed between steel rollers at 20 psi (1.379 x 10^5 N/m^2) dried against a heated metal surface. Disc cure time, five minutes.

Comparative Example 1

To a slurry of bleached hardwood kraft, bleached softwood sulfite, and second cut cotton linters at 4% consistency in water, 2% sodium carbonate, 4% calcium carbonate, 20% C.I. Leuco Sulfur Black 1 Dye, 12% ferrous sulfate heptahydrate, 15% sodium hydroxide and 1% melamine formaldehyde wet strength resin were added based upon pulp weight. This furnish was then diluted to 0.5% with water, adjusted to pH 8.0 with papermakers alum and formed into a fibrous mat by draining the suspension through a wire screen. The fibrous mat was then removed from the screen, placed between linter blotters, pressed between steel rollers at 20 psi (1.379 x 10^5 N/m^2) and dried against a heated metal surface. Disc cure time, three minutes.

Comparative Example 2

To a slurry of bleached hardwood kraft, bleached softwood sulfite, and second cut cotton linters at 4% consistency in water, 2% sodium carbonate, 4% calcium carbonate, 20% C.I. Leuco Sulfur Black 1 Dye, 12% ferrous sulfate heptahydrate, 20% magnesium hydroxide, 15% sodium hydroxide and 1% melamine formaldehyde wet strength resin were added based upon pulp weight. This furnish was then diluted to 0.5% with water, adjusted to pH 8.0 with papermakers alum and formed into a fibrous mat by draining the suspension through a wire screen. The fibrous mat was then removed from the screen, placed between linter blotters, pressed between steel roller at 20 psi (1.379 x 10^5 N/m^2) and dried against a heated metal surface. Disc cure time, two minutes, thirty seconds.

Claims

1. A decor sheet for use in a decorative laminate, said sheet including cellulosic fibres, a sulfur dye, and a precipitate of a basic salt.

2. A decor sheet according to Claim 1, wherein said salt is a hydroxide.

3. A decor sheet according to Claim 2, wherein said salt is an alkaline earth metal hydroxide, preferably magnesium hydroxide.

4. A decor sheet according to any preceding claim, wherein said salt is precipitated by ion exchange interaction of a first water soluble salt and a second water soluble salt of a strong base.

5. A decor sheet according to Claim 4, wherein said second salt is sodium hydroxide.

6. A decor sheet according to Claims 4 or 5, wherein said first salt is an alkaline earth metal surface or chloride, preferably magnesium sulfate or magnesium chloride.

7. A decor sheet according to any preceding claim, wherein said precipitated basic salt is present in said sheet in an amount of about 5 to 20% based on oven dry pulp.

8. A decor sheet according to any preceding claim, wherein said sheet exhibits a disc cure time of about 7 to 10 minutes.

9. A decorative laminate including a decor sheet according to any preceding claim.

10. A process for forming a decor sheet which comprises preparing a papermaking furnish of a cellulosic pulp, a sulfur dye, and a first water soluble and a second water soluble salt of a strong base, said first and second salts interacting to form a precipitate of a water insoluble basic salt; and forming a sheet from said furnish.

11. A method according to Claim 10, wherein said sulfur dye is added to said furnish as a leuco dye and said leuco dye is converted to its oxidized form.

12. A method according to Claim 10, wherein said sulfur dye is added to said furnish in its oxidized form, converted to its soluble leuco form by addition of a reducing agent and reconverted to its oxidized form to deposit the dye on the fibres in the furnish.

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EUROPEAN SEARCH REPORT

Application Number
EP 92 31 0904

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB-A-818 652 (ARMSTRONG CORK COMPANY) * page 1, line 13 - page 2, line 110 *	1-4,6,10	B44C5/04 D21H17/67 B32B27/04
A	GB-A-2 255 981 (SANDOZ LTD.) * page 2, paragraph 2 - page 12, paragraph 1 * * page 22, paragraph 4 - page 23, paragraph 2 *	1,11,12	
A	Derwent Publications Ltd., London, GB; AN 84-137429 & JP-A-59 071 333 (SHOWA DENKO ET. AL.) 23 April 1984 * abstract *	1-3,9,10	
A	EP-A-0 003 481 (THE DOW CHEMICAL COMPANY) * page 4, line 6 - page 5, line 20 * * page 10, line 13 - page 11, line 4 * * page 16, line 5 - page 16, line 25 *	1-3	
A	GB-A-2 225 794 (HOECHST AKTIENGESELLSCHAFT) * page 3, line 7 - page 6, line 14; example 1 *	10-12	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B44C C09B D21H D06P

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 JULY 1993	DOOLAN G.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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